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## Examining the effects of storage on the initiation behaviour of ionic liquids towards the cure of epoxy resins.

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**ABSTRACT:** Four structurally related ionic liquids (1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium diethyl phosphate, 1-ethyl-3-methylimidazolium dicyanamide, and 1-ethyl-3-methylimidazolium thiocyanate) are examined for their storage characteristics and its effect on their ability to initiate the cure of epoxy resins. At ambient temperature, epoxy formulations containing 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium thiocyanate display marked colour changes to yield dark red samples with greatly increased viscosity after one day; after six days both samples have undergone vitrification. The epoxy formulation containing 1-ethyl-3-methylimidazolium acetate continued to polymerise even at sub-zero temperatures. Storage in dark bottles retarded the reaction during the 30-minute period that the sample is removed from the freezer prior to an aliquot being taken, but once the autocatalytic low temperature reaction has started, the dark glass no longer provides effective protection. Samples of 1-ethyl-3-methylimidazolium dicyanamide/epoxy were also stored and sampled in the same manner, but no differences were exhibited between the samples in clear and dark brown glass bottles. Infrared and nuclear magnetic resonance studies confirmed that the hygroscopic ionic liquids pick up water readily (coordinating to the H atom at the 2-position on the imidazolium ring), but once dried the initiating ability is lost.

**Keywords:** Epoxy Resins, Ionic Liquids, Imidazoles, Initiators, Storage Stability.

## INTRODUCTION

Epoxy resins are especially interesting to the composites industry due to their design versatility and the wide variety of chemical compounds, which can effect cure [1], making it possible to tailor the level of cross-linking and the temperature at which the reaction is carried out [2]. Imidazoles have been demonstrated to catalyse the homopolymerisation of epoxide groups [3,4] and compositions of imidazoles and epoxy resins yield adhesives and coatings with very good mechanical properties and superior physical properties [5] such as better heat resistance [6], lower tensile elongation, and higher modulus. Imidazole formulations can offer a wider range of cure temperatures compared with amine-cured systems [7], but the reactivity of the imidazole can limit the processability of the formulations with relatively short processing windows. Ramis *et al.* [8] employed 1-methylimidazole to accelerate the Jeffamine-cured polycondensation of the diglycidylether of bisphenol A, but found that differences in reactivity (with diethylene triamine or hyper-branched poly(ethyleneimine)s) meant that the 1-methylimidazole was unsuitable for use in mixed formulations requiring sequential curing steps. A variety of strategies have been examined to control their reactivity, including the formation of coordination compounds [9]. Structurally related imidazolium-based ionic liquids [10] are relatively easily prepared [11] and offer good stability of the ring in oxidative and reductive environments. From the perspective of processing, ionic liquids act as catalysts to enhance both the rate of reaction and the reaction yield, but also offer low viscosity formulations.

The ability to display cure latency (*i.e.* to mix an epoxy monomer with a curing agent, hardener and store it at ambient or sub-ambient temperature without advancement of the reaction [12,13]) is a key feature of a one-pot formulation allowing ease of processing, ease of storage, cost reduction, and customer convenience. Kowalczyk and Spychaj [14] examined the use of 1-butyl-3-methylimidazolium tetrafluoroborate as an initiator for a commercial epoxy (Epidian 6) and additionally, a formulation comprising the two components could be stored for a period of 6 months at ambient temperature without any change in viscosity. Rahmathullah *et al.* [15] explored the use of 1-ethyl-3-methylimidazolium dicyanamide as an initiator for epoxy resins and, moreover, determined that it could be used as a latent initiator which was miscible with another commercial epoxy (Epon 828) and exhibited long-term stability at room temperature. The stability of the formulation was tracked through monitoring the characteristic epoxy ring absorbance band in near-infrared spectroscopy and it was suggested by the authors that the mechanistic route may involve reaction between the cyanamide and epoxy groups and not the nitrogen atoms in the imidazolium

cation directly.

Maka *et al.* also reported the use of imidazolium-based ionic liquids as initiators for epoxy resins based on both 1-decyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations with chloride, tetrafluoroborate and dicyanamide anions [16]. It was suggested that, in these cases, thermal decomposition of the ionic liquid could proceed *via* a highly stabilised N-heterocyclic carbene structure, which, in turn, would result in generation of imidazole or 1-alkyl derivatives. The interaction of the pyridine-type nitrogen atom in the imidazole ring with an epoxy group to form a 1:1 adduct was concluded as the most likely anionic polymerisation route. The stability of the formulations stored at room temperature was examined and revealed that samples comprising tetrafluoroborate exhibited a storage period of 20 days irrespective of the cation size, the viscosity of the 1-decyl-3-methylimidazolium chloride/diglycidylether of bisphenol A (DGEBA) system remained almost unchanged after a storage period of 30 days at room temperature; no influence of alkyl chain length on the storage time was identified. In a further study, Maka *et al.* found that the initiation of the epoxy polymerisation reaction with 1-butyl-3-methylimidazolium thiocyanate proceeded *via* thermal decomposition products including imidazole and alkyl derivatives resulting from the ionic liquid [17]. Soares *et al.* reported that N,N'-dioctadecylimidazolium iodide successfully initiated the polymerisation of DGEBA and also suggested that the mechanism proceeded *via* thermal decomposition of the ionic liquid at high temperatures to yield imidazole, N-alkylimidazoles and imidazole moieties linked by a methylene bridge which were capable of initiating the polymerisation reaction [18].

We have already reported our findings on the proposed initiation mechanism involving 1-ethyl-3-methylimidazolium acetate [19], and found that it degraded at 150 °C to yield dealkylated products including methyl acetate and ethyl acetate as well as 1-methylimidazole and 1-ethylimidazole. The dealkylated imidazole ring was proposed as a route for initiation of the epoxy ring. Adduct formation between 1-ethyl-3-methylimidazolium acetate and benzaldehyde at room temperature was observed leading to the proposal of the generation of a carbene species as a route for initiation of the epoxy ring in formulations with the acetate anion. At elevated temperatures, a second, competing reaction, involving deprotonation of the imidazolium ring, also becomes active. We have now extended the investigation into the ability of formulated epoxy/ionic liquid formulations to be stored at room temperature and at sub ambient temperatures is an important step to determine how this affects subsequent polymerisation reaction kinetics and mechanism. The present paper addresses the influence of initiator structure and storage temperature on latent cure capability.

## EXPERIMENTAL

**Instrumentation.** Infra-red spectra were obtained using an Agilent Technologies Cary 600 Series Fourier Transform Infrared spectrometer. A golden gate accessory with a diamond crystal was used for all ATR-IR spectroscopy analyses. A background spectrum consisting of 32 scans with the golden gate *in situ* was run before all analyses. The resulting spectrum for each sample was taken from an average of 32 scans which were recorded in absorbance mode over a spectral range of 600 – 4000  $\text{cm}^{-1}$ . The samples were placed directly on the sapphire platform and good contact between the diamond crystal and sample was checked prior to commencement of analysis. The data were processed using Agilent Resolutions Pro.

$^1\text{H}$  NMR spectra comprising of 16 scans, conducted on a Bruker 300 MHz nuclear magnetic resonance (NMR) spectrometer at room temperature. The samples for analysis (80 mg) were mixed with  $\text{D}_6$ -acetone (0.6 – 0.7 ml) and transferred to a NMR tube.

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples ( $5.0 \pm 0.5$  mg) in hermetically sealed aluminium pans. Experiments were conducted at a heating rate of 10 K/min. from  $-10\text{ }^\circ\text{C}$  to  $200\text{ }^\circ\text{C}$  (heat/cool/heat) under flowing nitrogen ( $50\text{ cm}^3/\text{min.}$ ). DGEBA and the ionic liquid were mixed by hand in glass scintillation vials. The samples were immediately analysed after mixing and the remaining mixture placed in the freezer. DSC analysis was also performed to study the differences in exothermic profile between freshly-mixed formulations and those which had been exposed to various storage periods and conditions. All analyses were performed at a scan rate of 10 K/min under a heat/cool/heat temperature programme from 0 –  $200\text{ }^\circ\text{C}$ .

Dynamic oscillatory rheology was performed using an Anton Paar MCR-300 rheometer with a 25 mm peltier plate and disposable aluminium pan set up. DGEBA and the ionic liquid were combined in a speed mixer pot (100 g) and subjected to two consecutive mixing periods of two minutes at 2500 rpm. The rheometer was operated in oscillation mode and samples were subjected to a temperature ramp from  $25\text{ }^\circ\text{C}$  to  $200\text{ }^\circ\text{C}$  at 5 K/minute with the collection of data set to a frequency of 0.2 minutes. The strain was held constant at 0.5 % and the normal force programmed to remain at 0 N.

**Materials.** The four ionic liquids (1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium diethyl phosphate, 1-ethyl-3-methylimidazolium dicyanamide, and 1-ethyl-3-methylimidazolium thiocyanate), and the diglycidyl ether of bisphenol A (DGEBA, Baxxores<sup>TM</sup> ER 2200,  $\text{eww } 182\text{ g/mole}$ ) were supplied by BASF (Fig. 1). The materials were initially characterised using  $^1\text{H}$  NMR (in deuterated acetone) and used without further purification (see

supplementary data, Fig. S1 and S2). 1-Methylimidazole (99 %) and phenylglycidylether (PGE, 99 %) were purchased from Sigma Aldrich and were used without further purification.

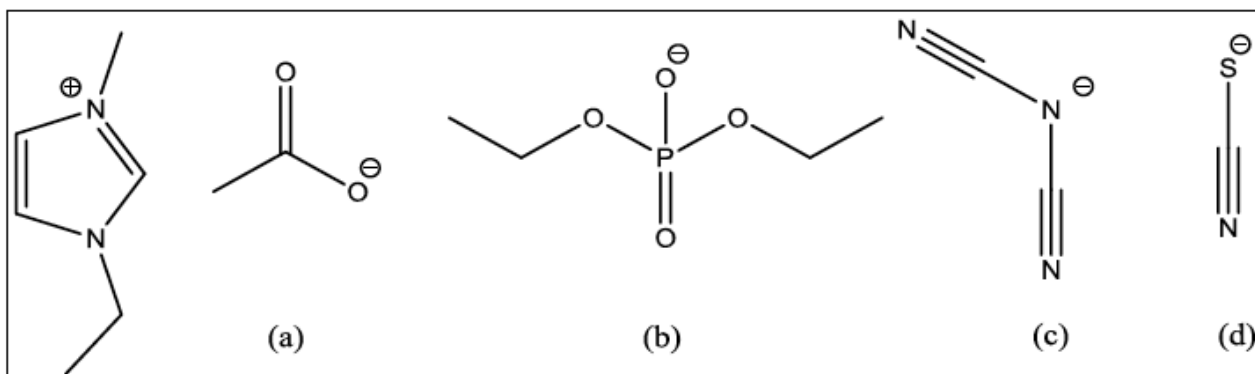


Figure 1. Structures of 1-ethyl-3-methylimidazolium (a) acetate, (b) diethyl phosphate, (c) dicyanamide, (d) thiocyanate.

#### *Preparation of freezer-stored formulations.*

Samples were prepared by mixing the ionic liquid (1 g) and the DGEBA (20 g) in clear scintillation vials (or dark glass bottles), which were then placed in the freezer. An aliquot of each sample (2-3 mg) was taken after the mixing period for immediate analysis, and all subsequent analyses were performed on aliquots that had been extracted from the bulk sample after equilibration at room temperature (30 minutes). The DSC analyses were performed using a heat-cool-heat cycle at a scan rate of 10 K/minute from 20 to 200 °C. A similar methodology was employed when using the formulations containing PGE (5 g) and 1-ethyl-3-imidazolium acetate (0.25 g). Samples were stored in clear glass vials; DSC analyses (5 –7 mg) were performed using a heat-cool-heat cycle at a scan rate of 10 K/minute from 20 to 140 °C. The use of PGE, a mono-functional model compound, enables the study of the polymerisation reaction without gelation. For rheological analysis, DGEBA was mixed with each ionic liquid using an automated mixer at a speed of 2500 rpm for two consecutive periods of 2 minutes. A sample was analysed immediately and the remaining material placed in storage at sub-zero temperatures. These samples were removed from the freezer and allowed to equilibrate at room temperature (30 minutes) prior to measurement.

#### *Preparation of formulations for water absorption study.*

A sample of 1-ethyl-3-methylimidazolium acetate was dried under vacuum at 40 °C for approximately 15 hours to rigorously remove water. The sample was subsequently divided between four glass scintillation vials, which had been stored in a drying oven for 24 hours prior to use, and left without a lid on in the fume cupboard. The samples were then weighed on a four-figure balance. Samples of the progressively exposed ionic liquid (0.05 g) were mixed with PGE

(1 g) to form a miscible blend and analysed using DSC at a scan rate of 10 K/min from 20 °C to 140 °C.

## RESULTS AND DISCUSSION

A series of samples was formulated (DGEBA 5 g + ionic liquid 0.25 g) in open aluminium pans (exposed to the atmosphere) and stored at ambient temperature (25 °C), with digital images collected periodically. After one day, samples containing 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium thiocyanate undergo marked colour changes to yield dark red samples with greatly increased viscosity (see supplementary data, Fig. S4); after six days both samples have undergone vitrification. The resulting colour change is representative of the degree of polymerisation as the polymers become increasingly aromatic and conjugated. In contrast, samples containing the diethyl phosphate and dicyanamide anions exhibit no marked colour changes, even after 6 days, indicating their lower reactivity.

The nature of the anions (and particularly the  $pK_a$  of the ionic liquid [19,16]) plays a pivotal role in determining the reactivity of the species towards carbene formation and hence initiation of the epoxy polyetherification reaction and also the storage stability. Reliable determination of  $pK_a$  is difficult and Millán *et al.* [20] sought to establish a  $pK_a$  scale for *N*-base amines in ionic liquids through use of a cyclic voltammetry method; they reported that in all cases the  $pK_a$  values obtained were greater than those obtained in aqueous solution. Carbene formation and thus polymerization is significantly more likely to occur in the acetate containing formulation, due to the higher Lewis base character of the acetate anion compared with the dicyanamide anion. DGEBA samples containing 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium thiocyanate both display a lower temperature peak (evident as a shoulder) in DSC thermograms (see Supplementary data, Fig. S3) [19], while those containing 1-ethyl-3-methylimidazolium dicyanamide exhibit two distinct exothermic peaks, and 1-ethyl-3-methylimidazolium diethyl phosphate shows an incomplete reaction under the scanning conditions used (demonstrating its low reactivity). These thermal data were used to yield a baseline for the subsequent storage studies, but although data were acquired for the samples incorporating the diethyl phosphate anion, for which the best storage stability was observed in an epoxy solvent at room temperature, they are not presented in the main text (but for completeness are included as supplementary information). The low reactivity of this particular ionic liquid towards the epoxy rendered it of little practical use as an initiator in the proposed application.

### *Examining storage stability in ambient stored formulations*

**DGEBA with 1-ethyl-3-imidazolium acetate.** DSC analysis was performed to study the

differences in exothermic profile between freshly-mixed formulations and those which had been exposed to various storage periods and conditions. The cure profiles reflect samples that were stored in a closed glass scintillation vial at ambient temperature for a period of nine days, during this time, the samples underwent vitrification to yield hard, solid materials (Fig. 2).

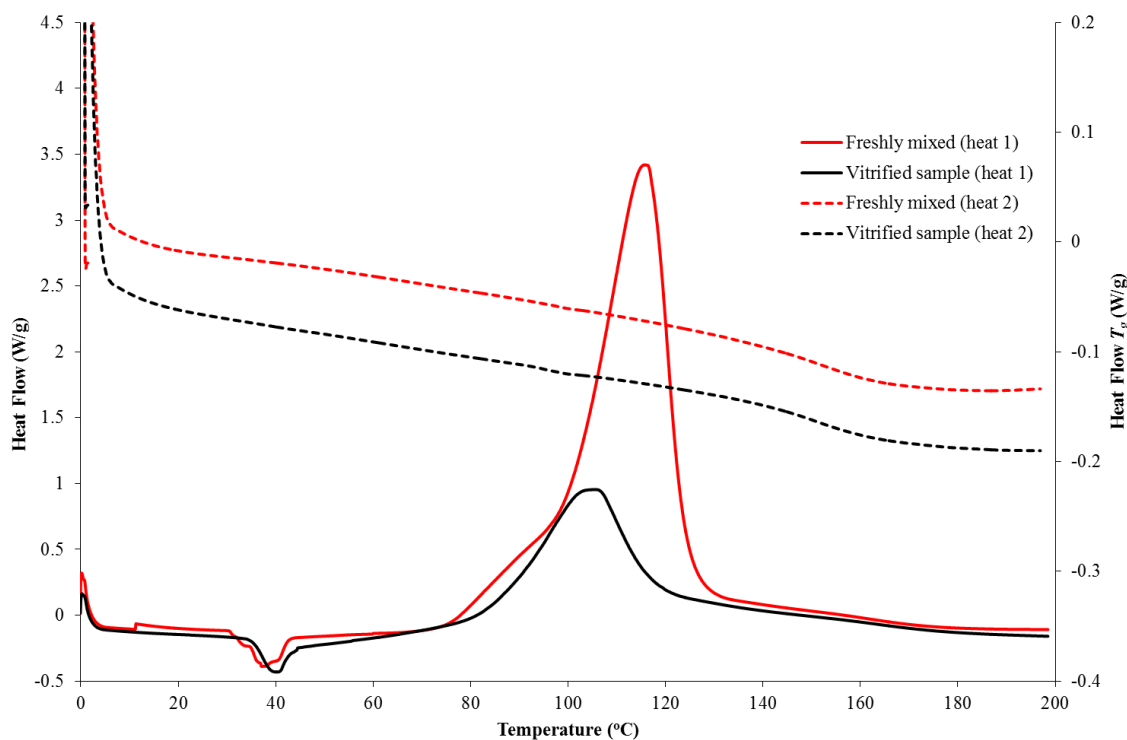


Figure 2. Comparison of dynamic DSC data for freshly-mixed (red) and vitrified (black) formulations of DGEBA (5 g) and 1-ethyl-3-methylimidazolium acetate (0.25 g)

After nine days at ambient temperature, the material has largely lost the low temperature peak and the overall enthalpy is considerably reduced (from 475 J/g / 86.5 kJ/mol. to 247 J/g / 44.9 kJ/mol.); a softening endotherm (30 °C) is still present. The vitrified sample is observed to commence reaction earlier than the freshly mixed sample and, despite remaining solid, still has an exothermic peak in a similar position to that for the freshly mixed sample. This suggests that the shoulder represents an essential prerequisite step, which is responsible for initiating the remaining reaction. Dynamic oscillatory rheology was performed on freshly-mixed samples of DGEBA (20 g) and 1-ethyl-3-imidazolium acetate (1 g), which were mixed and stored at room temperature. Both the gel point and the vitrification point fall steadily with increasing storage time, while over the storage period the viscosity of the sample rose (Fig. 3). In all cases, the storage moduli are all similar, which implies that the networks formed are similar.



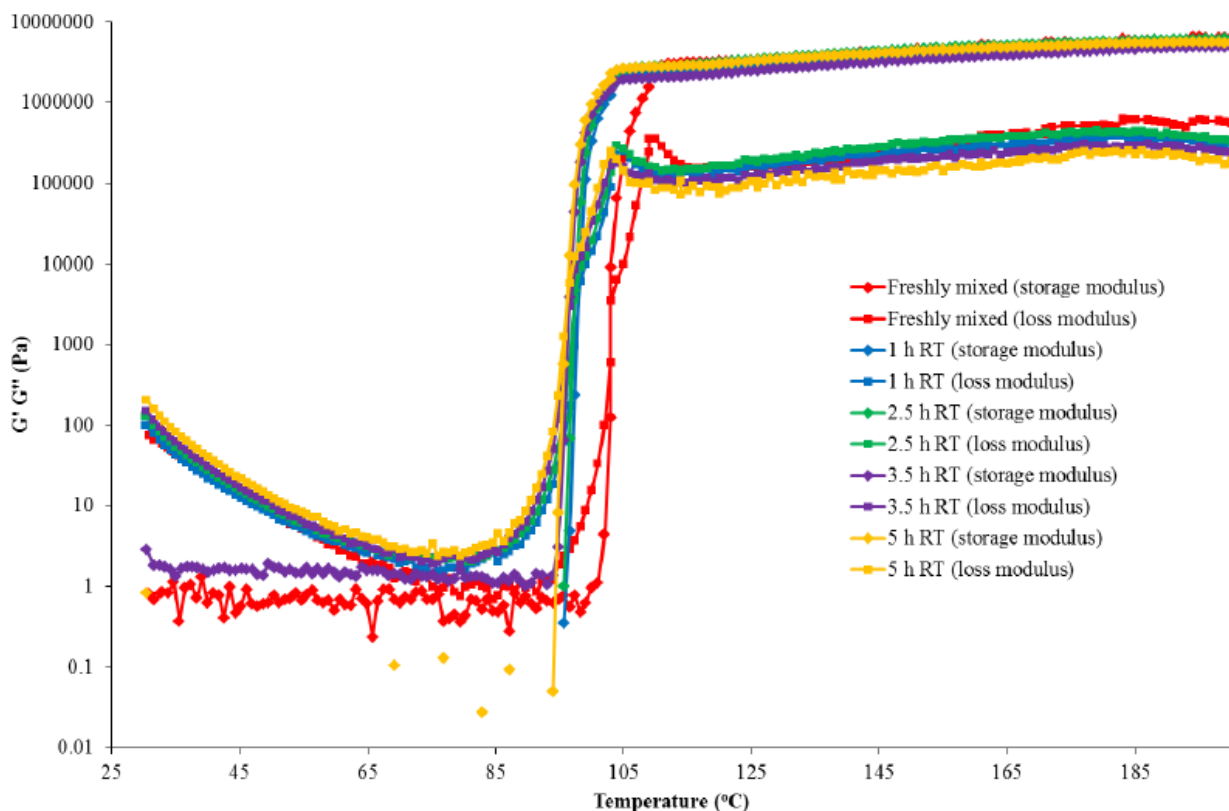


Figure 3. Dynamic oscillatory rheology data for stored formulations comprising DGEBA (20 g) and 1-ethyl-3-imidazolium acetate (1 g) as a function of storage time.

As the concentration of 1-ethyl-3-methylimidazolium acetate is increased (to 3 g in the formulation, resulting in a more fluid mixture), the gel point is marginally reduced after storage (1 hr) (Table 1) and is accompanied by a drop in the storage modulus and an increase in viscosity from 7 to 15 Pa.s. Furthermore, this is accompanied by the appearance of two discrete peaks in the storage modulus response.

Table 1. Dynamic oscillatory rheology data for stored formulations comprising DGEBA (20 g) and different ionic liquids as a function of composition, storage temperature and storage time.

Ionic liquid	Mass (g)	Storage temp. (°C)	Storage time (hr)	Gel Point (°C)	T <sub>vit1</sub> (°C)	T <sub>vit2</sub> (°C)	Viscosity (Pa.s)
1-ethyl-3-methylimidazolium acetate	1	-5	0	103	110	-	8
			1	98	105	-	10
			2.5	98	104	-	13
			3.5	97	103	-	15
			5	-	-	-	20

			168	103	110	-	-
			336	99	107	-	-
			504	98	106	-	-
		25	0	103	110	-	8
			1	98	105	-	10
			2.5	98	104	-	13
			3.5	97	103	-	15
			5	96	103	-	20
	3	-5	0	101	105	130	7
			168	101	105	129	-
			336	96	101	124	-
		25	0	101	105	130	7
			1	-	-	-	15
			2	96	101	126	-

dicyanamide	1	25	0	165	185	-	3
			672	157	180	-	6
	5		0	156	-	-	2
			168	155	-	-	2
			336	152	-	-	2
			504	152	-	-	2
			672	150	-	-	2

thiocyanate	1	-5	0	112	117	-	8
			168	109	115	-	-
			336	109	115	-	-
			504	109	115	-	-

Key: - not determined

**DGEBA with 1-ethyl-3-imidazolium dicyanamide.** The rheological data (Table 1) show that, compared with the other ionic liquids studied, the initiation reaction occurs at a higher temperature, and the moduli values at the gel point and at the conclusion of the analysis are markedly lower when the dicyanamide is used. The increase in viscosity of the formulation occurs slowly, from 3 Pa.s to 6 Pa.s over a period of one month, with no obvious indication of vitrification, confirming the latent curing ability of this initiator and its suitability for use in one-pot formulations. The concentration of the ionic liquid was increased fivefold and, while the reaction is accelerated and

the gel point temperature is steadily reduced as the storage time increases, the viscosity of the formulation does not increase markedly (remaining lower than the formulation containing 1 g of ionic liquid after four weeks of storage).

#### *Examining storage stability in freezer stored formulations*

**DGEBA with 1-ethyl-3-imidazolium acetate.** The DSC data for the formulations during storage in the freezer (Table 2) demonstrate that following an extended period of storage (74 days), the low temperature peak at 90 °C had been considerably reduced in size (Fig. 4), confirming that the activation of the ionic liquid continues even at sub-zero temperatures. The softening endotherm, observed in Fig. 2, is not seen in this formulation, but the resulting initiation/polymerisation behavior is practically identical for the freshly mixed samples (heat 1). The glass transition temperature for the same formulation increased during the early stages of the storage period (see supplementary data, Fig. S5).

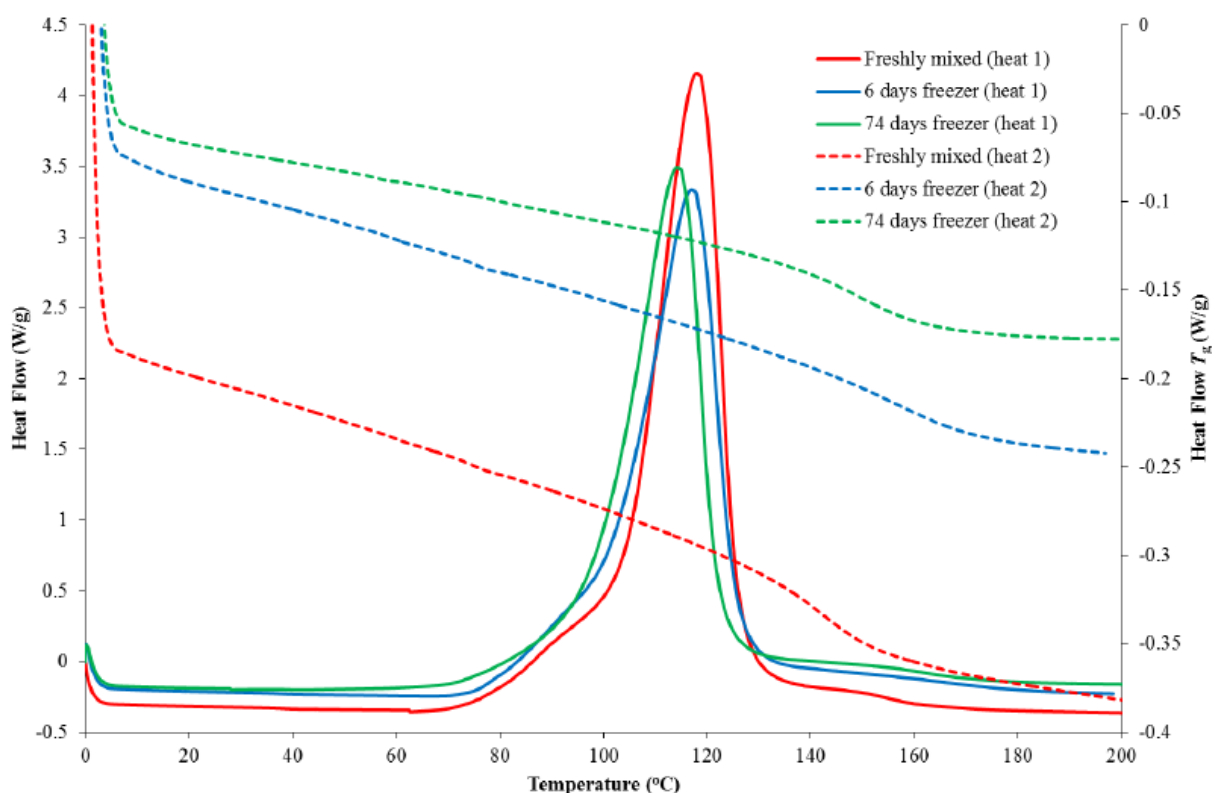


Figure 4 Comparison of dynamic DSC data for freezer stored formulations of DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (0.25 g) as a function of storage time. *N.B.*, Freshly mixed (red) formulation (red), following 6 days (blue) and 74 days storage (green) in the freezer.

Table 2 Comparison of dynamic DSC data for freezer stored formulations of DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (0.25 g) as a function of storage time.

Storage time (days)	$T_o$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)	$\Delta H_p$ J/g (kJ/mol.)	$T_g$ (°C)
0	64	114	187	475 (86.5)	151
3	62	115	188	483 (87.9)	158
14	64	116	187	449 (81.7)	153
24	68	116	190	479 (87.2)	154
30	65	114	191	475 (86.5)	158
52	64	113	194	455 (82.8)	161
301	68	115	187	427 (77.7)	155

Key:  $T_o$  = temperature of onset of polymerisation exotherm;  $T_{max}$  = temperature of maximum of polymerisation exotherm;  $T_f$  = temperature of endpoint of polymerisation;  $\Delta H_p$  = enthalpy of polymerisation;  $T_g$  = glass transition temperature.

The DSC data for samples stored in the freezer throughout the storage period (301 days) are shown overlaid (Fig. 5), and an expansion of the low temperature peak is shown offset for clarity. The positions of the exothermic peak maxima ( $T_{max}$ ) and the onset of polymerisation ( $T_o$ ) do not change significantly during the storage period. The loss modulus is reduced during the early stages of the reaction (Fig. 6), due to the reduction in sample viscosity as a function of temperature. The storage modulus remains constant during the first part of the reaction for the freshly-mixed sample, but after three weeks, the gel point has decreased from 103 °C to 98 °C and the vitrification point from 110 °C to 106 °C respectively.

A second series of samples was stored in dark brown glass bottles, to reduce the effects of sunlight/UV radiation. The DSC data obtained (Fig. 7, see supplementary data, Figs. S6 and S7) showed very similar behaviour to the samples stored in clear glass, but a difference in the exothermic response is observed after 14 days of storage (the shoulder is lost in the sample stored in a clear glass bottle). After 24 days, the shoulder in the sample stored in the dark glass bottle has almost disappeared, and by day 30 both samples follow an almost identical curve. This suggests that the dark bottles aid in retarding the initiation reaction during the 30-minute period that the sample is removed from the freezer prior to an aliquot being taken. It is probable that after the autocatalytic low temperature reaction has started, the dark glass no longer provides effective protection. No differences were observed for samples of 1-ethyl-3-methylimidazolium dicyanamide/DGEBA stored and sampled in clear and dark brown glass bottles.

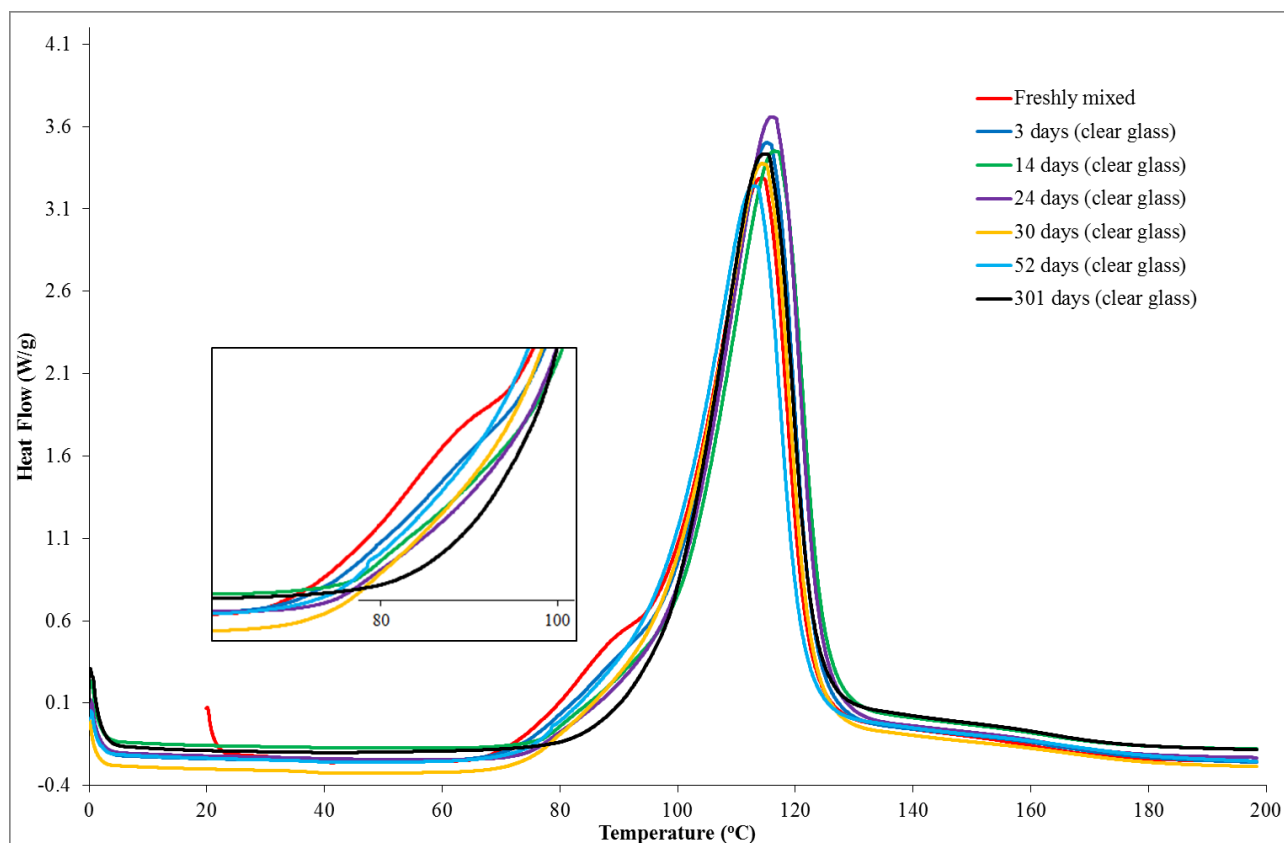


Figure 5. Dynamic DSC data (heat 1) for freezer stored formulations of DGEBA (20 g) and 1-ethyl-3-imidazolium acetate (1 g).

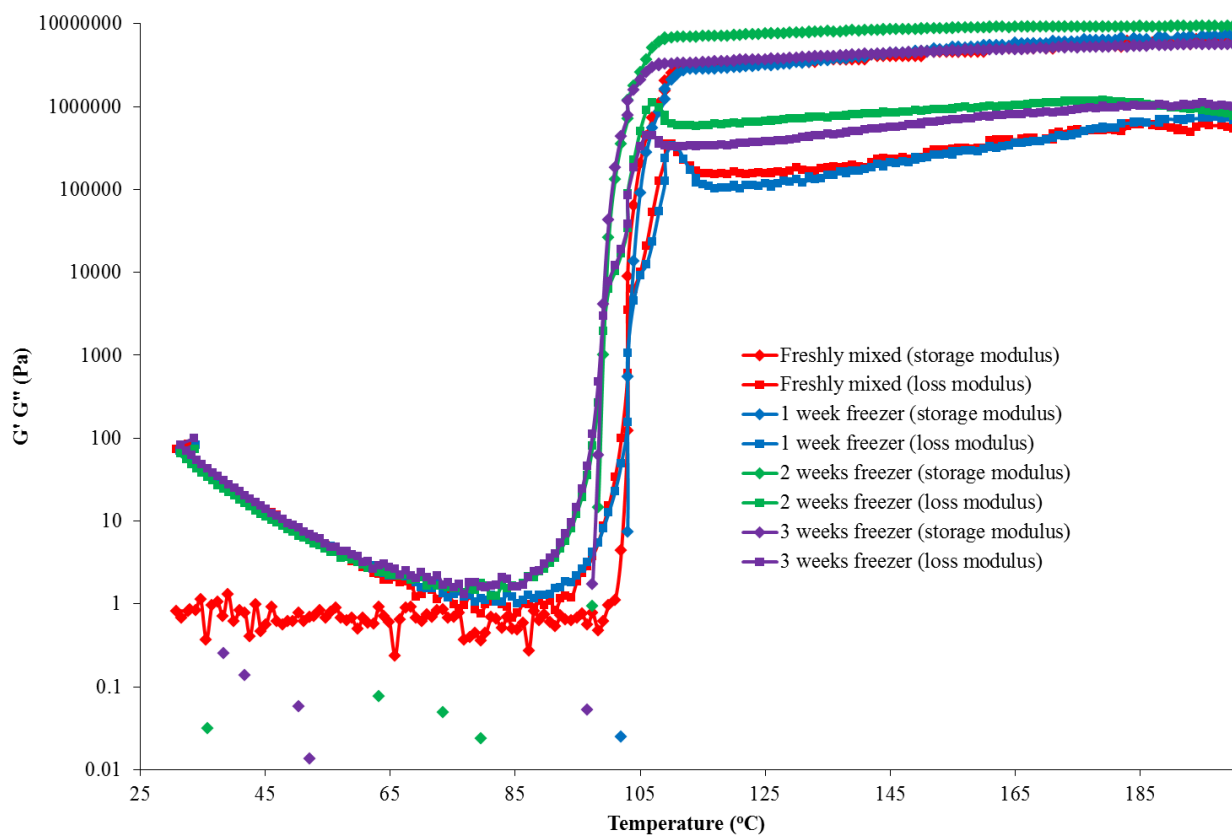


Figure 6. Dynamic oscillatory rheology data for freezer stored formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g)

DSC data for the formulations containing 1-ethyl-3-methylimidazolium dicyanamide/DGEBA and 1-ethyl-3-methylimidazolium diethylphosphate/DGEBA are given in the supplementary data, Figs. S8, S9, and S10).

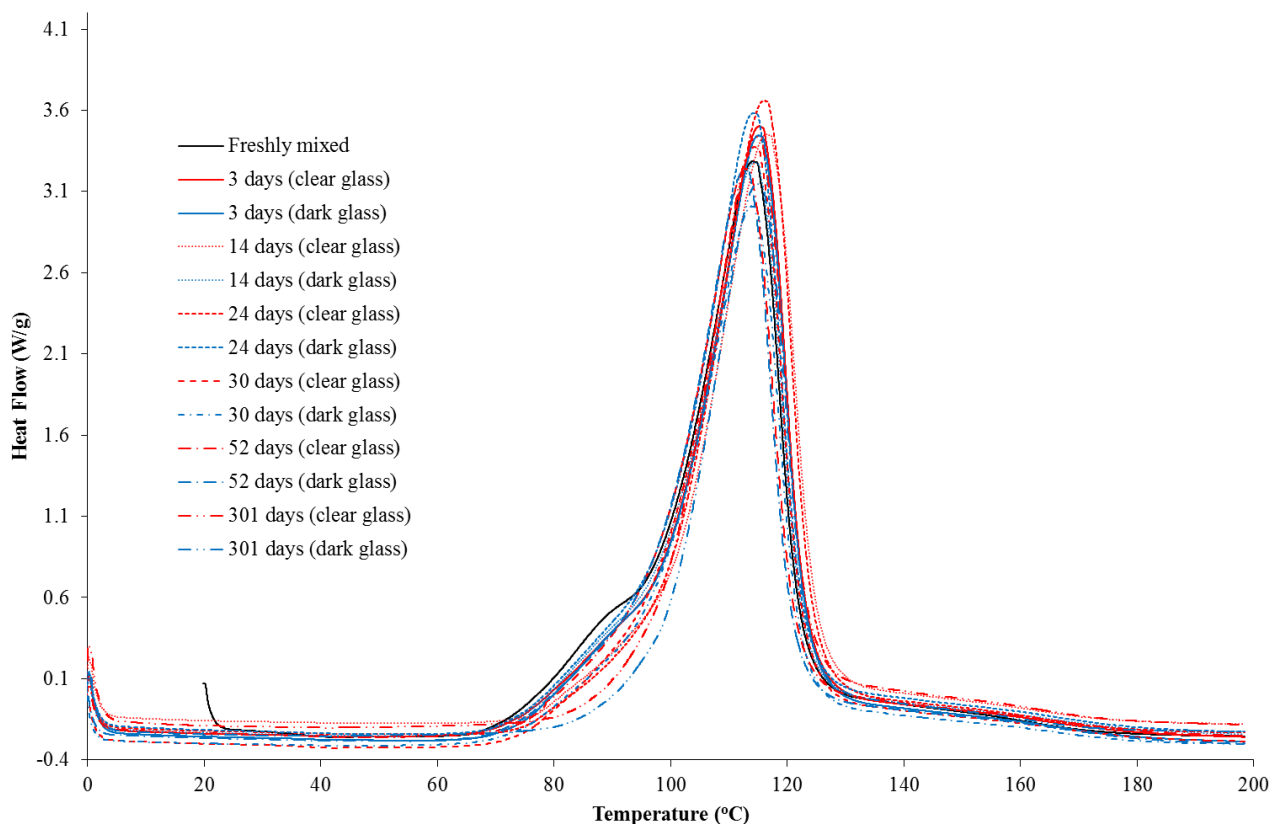


Figure 7. Dynamic DSC data (heat 1) for freezer stored formulations of DGEBA (5 g) and 1-ethyl-3-imidazolium acetate (0.25 g) in clear glass (red data) and dark bottle (blue data).

**PGE with 1-ethyl-3-imidazolium acetate.** The freezer study was repeated using a formulation containing the model compound PGE (5 g) and 1-ethyl-3-imidazolium acetate (0.25 g), to probe the disappearance of the low temperature, ring-opening reaction that constitutes the shoulder. While the data (Fig. 8) appear more scattered than for samples mixed with DGEBA, and the exothermic peaks were not quantified due to the unreliability of the baseline, it is still possible to observe the loss of the low temperature peak. In the freshly mixed sample there is a clear plateau between 90-99 °C, which can also be seen in the 2, 3, and 9-day samples. This region is no longer visible in the 10 day sample and an unusual drop in heat flow, which might represent a  $T_g$ , is visible in the 30 day sample possibly due to the advancement of the reaction during the storage period.

**DGEBA with 1-ethyl-3-imidazolium thiocyanate.** The DSC thermogram (Fig. 9) exhibits a similar profile to the 1-ethyl-3-imidazolium acetate formulation, with a low temperature shoulder on the main peak and a small, broad peak suggesting a high temperature reaction.

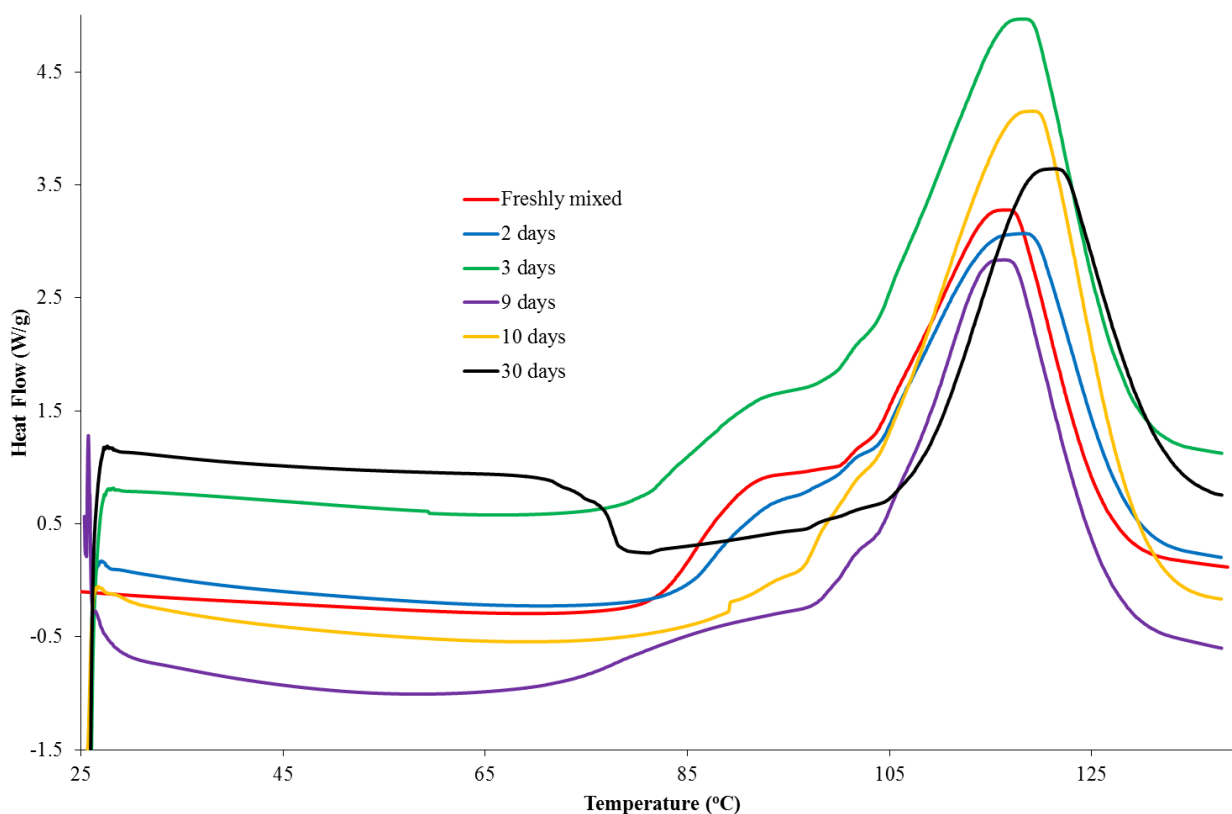


Figure 8. Comparison of dynamic DSC data for freezer stored formulations of PGE (5 g) and 1-ethyl-3-methylimidazolium acetate (0.25 g) as a function of storage time.

The onset of the reaction does not occur until approximately 82 °C, which is higher than the acetate systems and the considerably steeper gradient suggests that the initiation reaction and main propagation reaction probably occur almost simultaneously. When the stored sample is compared with the freshly blended formulation the low temperature shoulder is greatly reduced and the onset of the reaction occurs at a much lower temperature (in common with the acetate), although the high temperature peak remains at the same temperature for both samples. The peak maximum ( $T_{\max}$ ) and the  $T_g$  do not shift appreciably between both samples indicating that the storage impacts the initial reaction, but not the overall propagation reaction. Over seven days the temperature of the gel point falls by 3 °C compared with the freshly-mixed sample, but there is no further change observed, which implies that the species responsible for the advancement of the reaction, whose exact nature is not known at this stage, forms quickly.

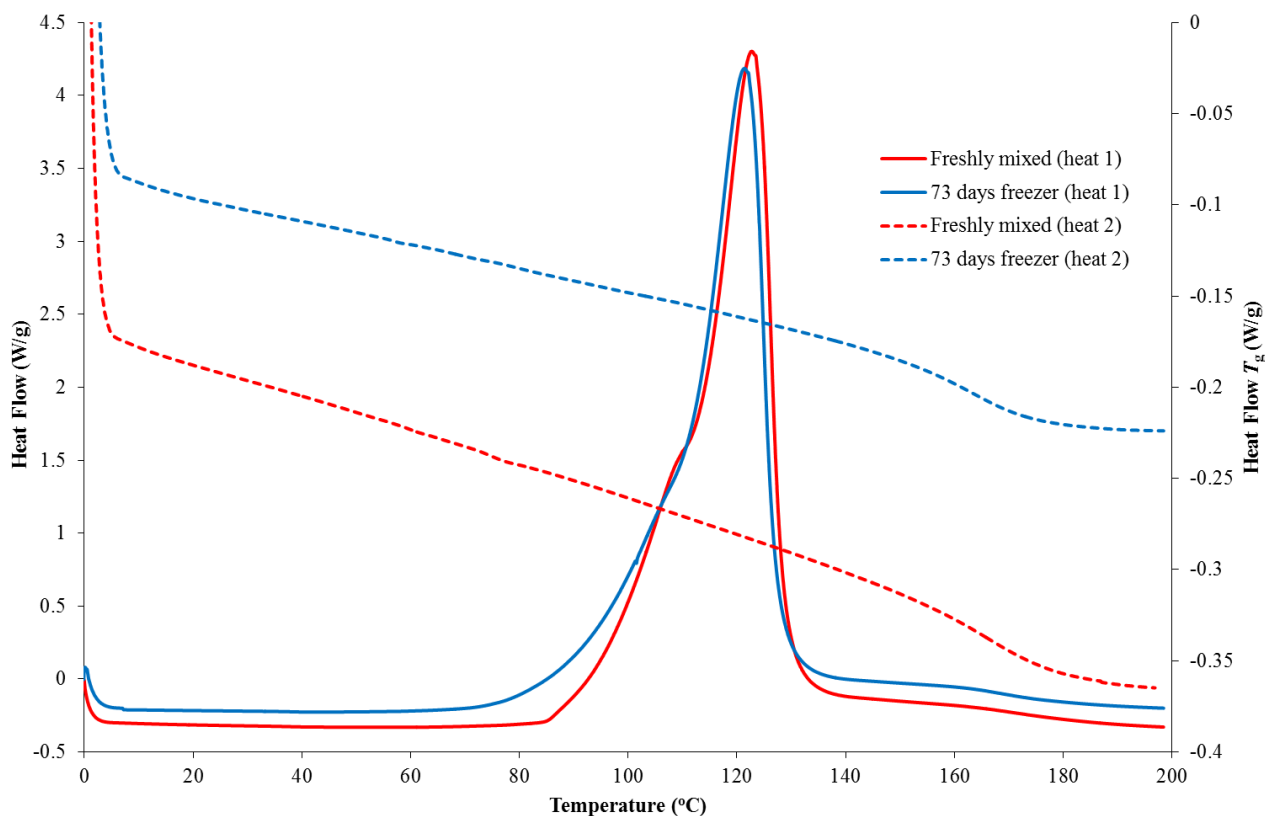


Figure 9. Dynamic DSC data (heat 1 and heat 3) for freezer stored formulations comprising DGEBA (5 g) and 1-ethyl-3-methylimidazolium thiocyanate (0.25 g).

A formulation containing a conventional initiator (DGEBA, 5 g, 1-methylimidazole, 0.25 g) was also included in the freezer storage study as a baseline comparison and the data are given as supplementary information (Fig. S11, Table S1). In accordance with reports by Heise and Martin [12], the DSC thermogram exhibits a single exothermic peak due to the nucleophilic attack of the unsubstituted nitrogen on the less-substituted methylene carbon of the oxirane ring to yield an alkoxy adduct (there is no potential route to the formation of a carbene). Fernández-Franco *et al.* reported that 2 parts per hundred parts resin (phr) of 1-methylimidazole was not sufficient to completely cure a DGEBA oligomer with a molecular weight of 364 g/mol [21], but Ooi *et al.* reported complete cure with an DGEBA oligomer with MW = 381 g/mol [22], when examining the differences in curing behaviour observed for three structurally-related imidazoles (containing 1-methyl-, 2-methyl-, and 2-phenyl- substituents) of steric *versus* inductive effects. It has been found that as the molecular weight of the DGEBA oligomer is raised, the reaction rate and the degree of conversion achieved both increase leading the researchers to conclude that the hydroxyl content in the DGEBA oligomer plays a major role on the reaction rate and also the conversion. For reference, in the present work, the study was carried out on a commercial epoxy with EEW 182 g/mol.



**Investigation into the Effect of Water on Ionic Liquids.** A spectroscopic study was carried out to examine the impact of water absorption on the ability of the ionic liquids to initiate the epoxy polymerisation. In the case of 1-ethyl-3-methylimidazolium acetate, the evolution of peaks corresponding to water molecules can be observed over the analysis period (Fig. 11). The emergence of a broad peak in the region  $3200 - 3300\text{ cm}^{-1}$  is indicative of the symmetric and asymmetric stretching modes of water. The broad peak appears to show two peak maxima as the exposure time is increased which are separated by approximately  $100\text{ cm}^{-1}$ . In addition, a peak emerges at approximately  $1627\text{ cm}^{-1}$ , which is attributable to the bending mode [23].

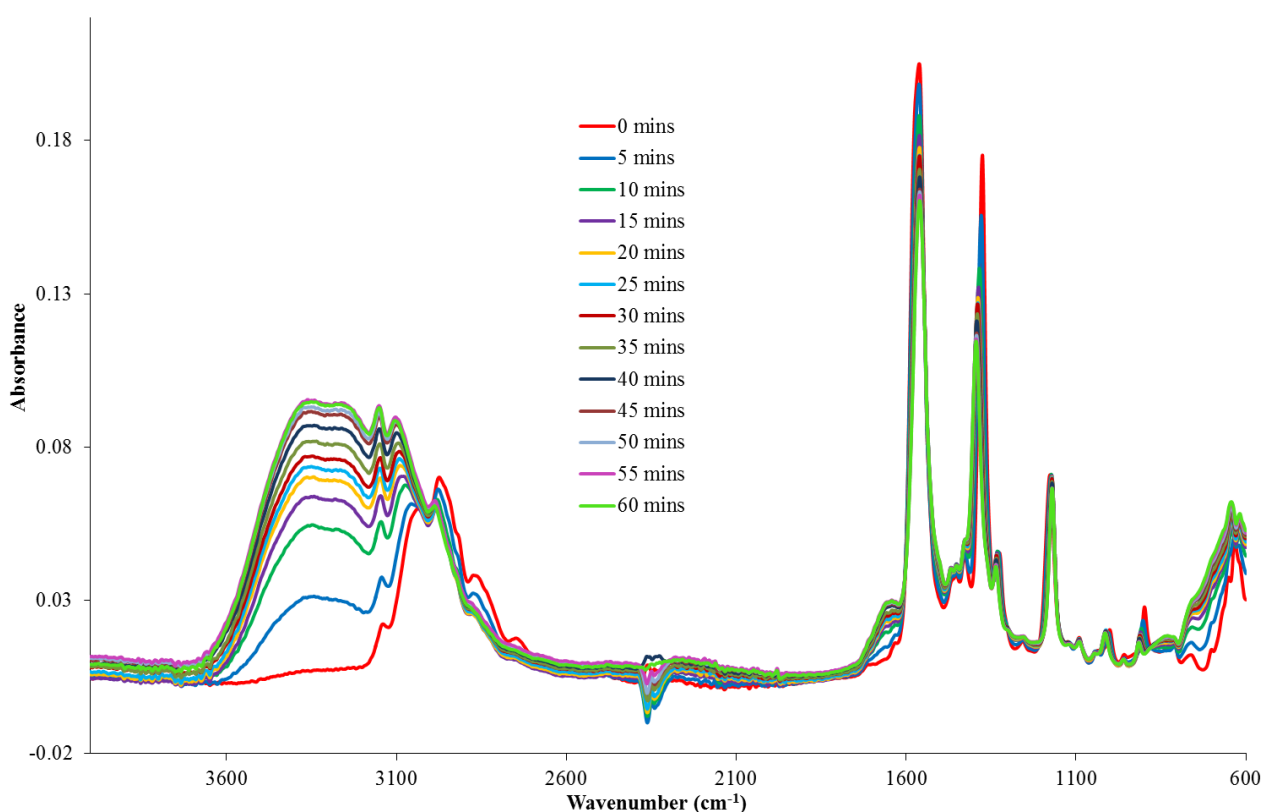


Figure 10. ATR-IR spectra of dried samples of 1-ethyl-3-methylimidazolium acetate following atmospheric exposure (up to 1 hour).

DGEBA formulations containing 1-ethyl-3-methylimidazolium diethyl phosphate and 1-ethyl-3-methylimidazolium thiocyanate display a growing peak at  $3350\text{ cm}^{-1}$ , which does not exhibit two peak maxima (see supplementary data, Figs. S12, S13, and S14), possibly due to broadening and merging due to hydrogen bonding; the bending vibration of the water molecules emerges at  $1640\text{ cm}^{-1}$ . These data are in agreement with the results of Cammarata *et al.* [23], who performed *in situ* studies using ATR-IR spectroscopy, with either 1-butyl-3-methylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium trifluoroacetate. Hall *et al.* [24] studied the effect of spiking a sample of 1-ethyl-3-methylimidazolium acetate with different quantities of water to investigate the effect

on the chemical shifts of the protons observed in the  $^1\text{H}$  NMR spectrum; all ring protons moved to a more upfield position with the acidic proton between the two nitrogen atoms showing the greatest movement in terms of its shift. A similar approach was followed in the present work by analysing the  $^1\text{H}$  NMR spectrum of a sample of 1-ethyl-3-methylimidazolium acetate after exposure in an open glass scintillation vial for a period of 90 minutes (Fig. 11); the corresponding  $^{13}\text{C}$  spectra are shown in the Supplementary data, Fig. S15. The presence of a new shift at approximately 4.0 ppm (denoted with an asterisk in Fig. 11) is assumed to result from water uptake by the ionic liquid. The ring protons experience an upfield shift with the most acidic proton exhibiting the greatest shift although the other peaks are unaffected. As the sample was not spiked with water the effects experienced by the protons will be significantly less than the previous report [24],

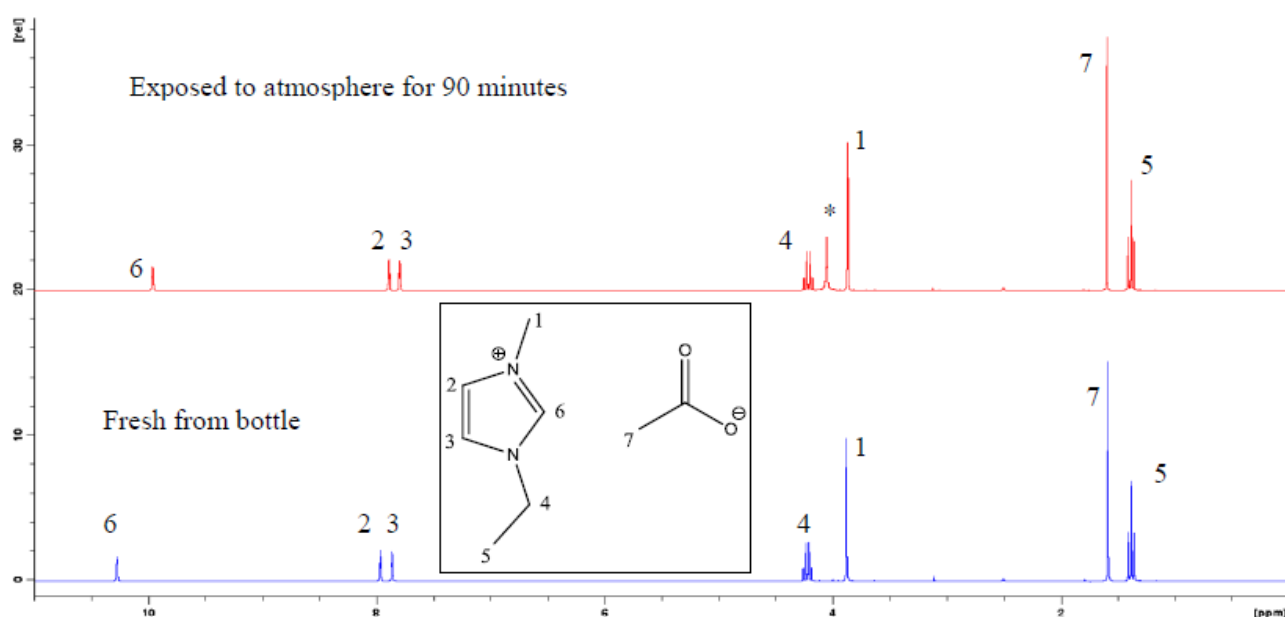


Figure 11.  $^1\text{H}$  NMR spectral data for 1-ethyl-3-methylimidazolium acetate (fresh from the bottle) and following atmospheric exposure (90 minutes).

The COSY spectrum (Fig. 12) reveals the coupling of protons 2 and 3 (protons on the imidazolium ring) with proton 1 (methyl group on imidazolium ring) and coupling of protons 4 (methylene group) and 1 (methyl group on imidazolium ring) with 5 (methyl group on alkyl chain). The proton at the 2-position on the imidazolium ring (referred to as proton 6) interacts with a number of other protons (1, 2, 3, 4, as well as the unidentified peak). Ficke *et al.* [25] reported a strong interaction between the acidic hydrogen at the 2-position on the ring and water, while Hall *et al.* interpreted similar results to indicate that the hydrogen bonded network of the ionic liquid had been disrupted by the addition of water molecules which formed strong hydrogen bonds between the anion in the ionic liquid resulting in the upfield shift of the ring protons.

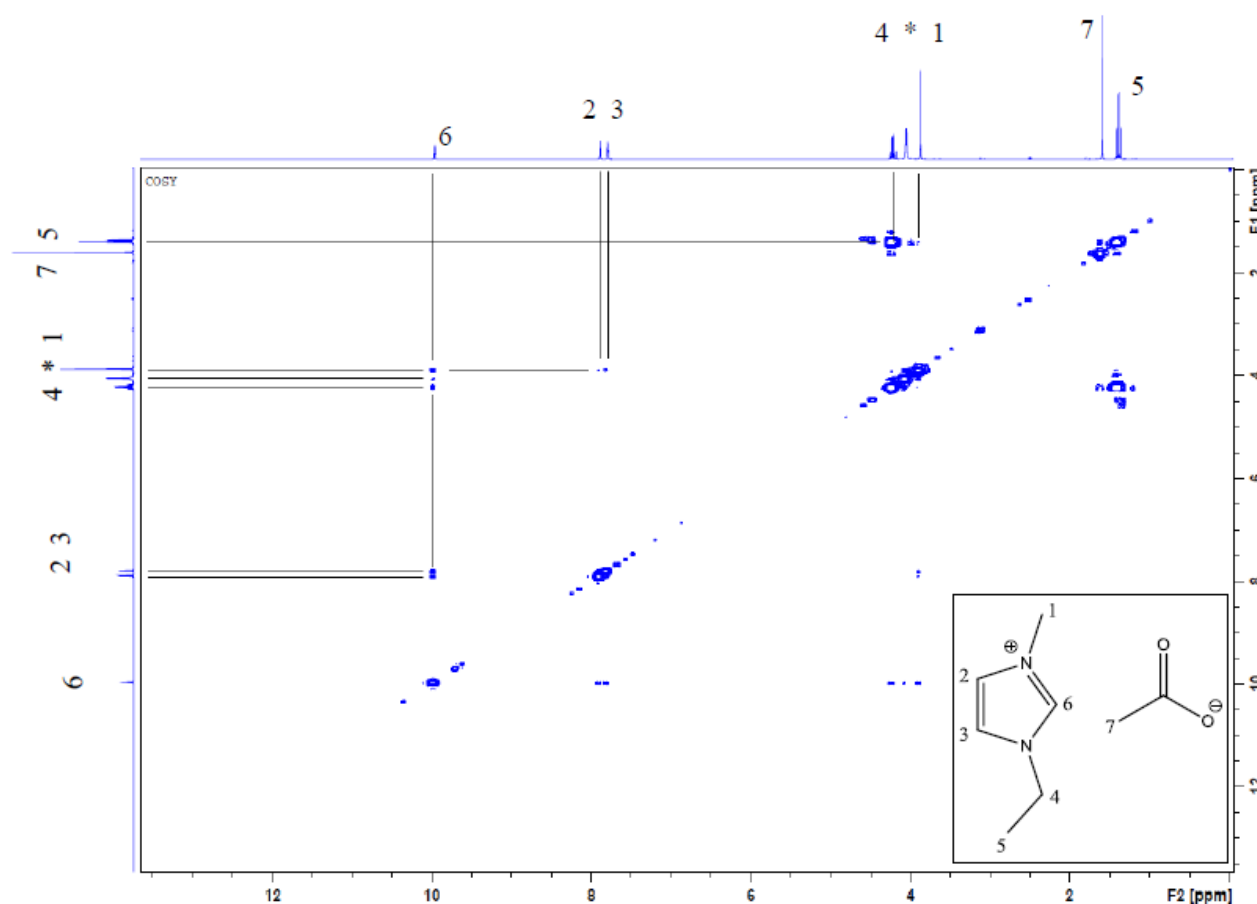


Figure 12.  $^1\text{H}$  NMR COSY spectrum of 1-ethyl-3-methylimidazolium acetate following exposure to the atmosphere.

In common with other imidazolium-based ionic liquids, 1-ethyl-3-methylimidazolium acetate is highly hygroscopic and drying under vacuum at 40 °C for approximately 15 hours was required to rigorously exclude water. The dried sample was then exposed to the atmosphere, weighed periodically (Table 3), analysed using ATR-IR spectroscopy, and then combined with PGE for DSC analysis (Fig. 13). Following exposure the PGE/1-ethyl-3-methylimidazolium acetate blend displays no exothermic peaks, confirming that the initiating ability of the ionic liquid had been lost, which is attributed to the ability of the material to support hydrogen bonding and proton abstraction. A freshly dried 1-ethyl-3-methylimidazolium acetate sample, which had not been exposed to the atmosphere, was analysed in a PGE blend using DSC. The onset of the reaction was considerably delayed and the peak maximum ( $T_{\text{max}}$ ) was shifted to a higher temperature than the sample that was taken freshly from the bottle, the loss of water would otherwise catalyse the etherification mechanism in the later stages of the reaction.

Table 3. Water absorption behaviour of 1-ethyl-3-methylimidazolium acetate as a function of exposure time

	Exposure Period (days)		
	2	3	6
Initial weight (g)	14.25	14.48	14.33
Final weight (g)	14.61	15.05	14.98
Difference (g)	0.36 (2.5 %)	0.57 (3.9 %)	0.65 (4.5 %)

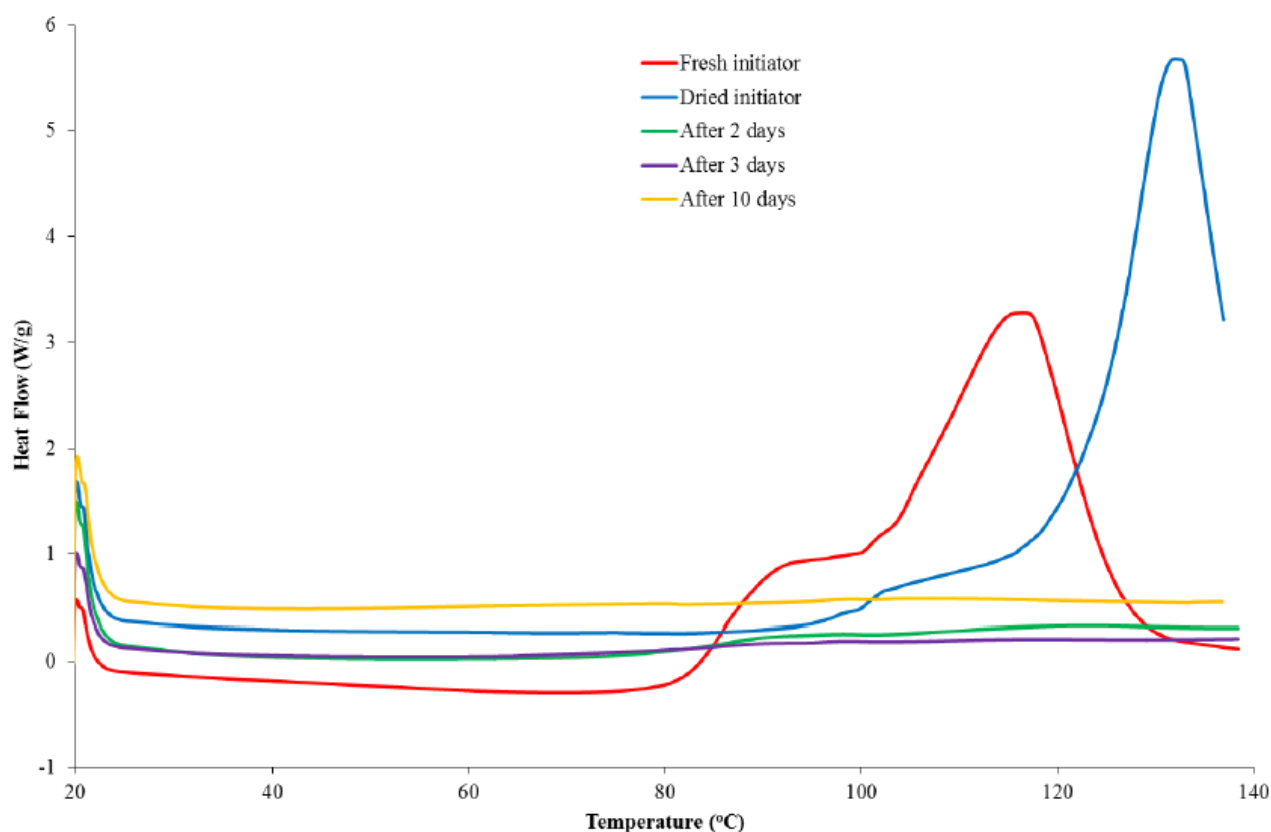


Figure 13. Dynamic DSC data for formulations comprising PGE (1 g) and dried and exposed 1-ethyl-methylimidazolium acetate (0.05 g)

The ATR spectra of the progressively exposed sample of 1-ethyl-3-methylimidazolium acetate displays an emerging broad bands at  $3400\text{ cm}^{-1}$  (O-H stretch) and  $1635\text{ cm}^{-1}$  (O-H bending mode) as evidence of water absorption as a function of exposure time. This is accompanied by loss of the large, multi-modal peak present in the fresh and dried samples, which is characteristic of the overlapping CH stretching modes in the imidazolium ring ( $3100\text{--}2600\text{ cm}^{-1}$ ). Additionally, the C-CH<sub>3</sub> stretching mode and the CH<sub>3</sub> bending mode in the acetate anion ( $1245\text{ cm}^{-1}$  and  $1423\text{ cm}^{-1}$  respectively) are lost in the samples that have been exposed to the atmosphere. The acetate anion bonds very strongly with the H atom at the 2-position on the imidazolium ring (Fig. 12) and in some

cases, the C2-H2 bond in the imidazolium ring is broken and the proton abstracted by the acetate anion to form acetic acid and a carbene. When water is incorporated into the system during exposure, the distance between the H atom at the 2-position on the ring and the oxygen atom of the acetate anion is increased preventing both proton abstraction and carbene formation [26]. If the acetate anion also preferentially forms hydrogen bonds with the water molecules and does not favour formation of carbenes, then the ring-opening reaction of the epoxy ring would also be severely hindered. Literature studies suggest that the acetate anion, when paired with the 1-ethyl-3-methylimidazolium cation, has the highest hydrogen bond acceptor value of  $>1.00$  followed closely by the diethyl phosphate anion which has a reported value of 1.00 [27]; the thiocyanate and dicyanamide anions have reported values of 0.71 and 0.64 respectively. Therefore it would be interesting in a future study to compare the effect of water on the initiating ability of the dicyanamide anion as this may be affected to a lesser degree due to the lower hydrogen bond acceptor ability value.

## CONCLUSIONS

The diglycidyl ether of bisphenol A is blended with four ionic liquids based on the 1-ethyl-3-methylimidazolium ion. The acetate and dicyanamide are the more reactive due to their  $pK_a$  values; while the thiocyanate is less reactive (and the diethylphosphate is of little practical use in this application). The effect of ambient and sub-zero storage on the loss of a low temperature peak (in the DSC thermogram) is studied and this is identified as representing an essential prerequisite step, in the initiation of the epoxy polymerisation reaction. The absorption of water has a profound effect on the initiating ability of the ionic liquid; a previously dried sample of 1-ethyl-3-methylimidazolium acetate, which had subsequently been exposed to the atmosphere for a number of days before being mixed with PGE, was rendered incapable of initiating the polymerisation reaction. Whilst it would be assumed that the hydroxyl groups present, as a result of water uptake, would be able to catalyse the etherification reaction, the lack of this initiating ability has been attributed to the preferential interaction of the water molecules with the acetate anion and the interaction of the water molecules around the acidic hydrogen.

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The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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